

DECREASED BENZENE EVAPORATIVE EMISSIONS FROM AN OXYGENATED FUEL

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ABSTRACT

A chromatographic head-space analysis was developed to determine the vapor phase concentrations of non-oxygenated and oxygenated fuels. The effect of ether oxygenates on benzene evaporative emissions was evaluated. A base fuel and three oxygenated fuels were prepared to contain 1 volume percent benzene at matched volatility levels. Head-space composition for each blend was measured, as a function of temperature, to determine the effects of oxygenates on benzene volatility. Results indicate MTBE (methyl *tert*-butyl ether), ETBE (ethyl *tert*-butyl ether), and TAME (*tert*-amyl methyl ether) each reduce benzene vapor phase concentrations. Benzene reductions averaged approximately 14 percent for fuels containing 2.7 weight percent oxygen. Reductions were temperature dependent, but not generally dependent upon type of ether oxygenate. Significant environmental benefits result from reducing benzene volatility and the resulting decrease in evaporative emissions. Benzene is classified by the EPA as a known human carcinogen. The 1990 Clean Air Act Amendments require reductions in gasoline benzene levels to reduce toxic emissions.

INTRODUCTION

The 1990 Clean Air Act Amendments require that gasoline sold in nine of the nation's most polluted cities be reformulated to produce less pollutant emissions. Beginning in 1995, reformulated gasoline will produce 15% less hydrocarbon emissions and regulated toxins. Hydrocarbon emissions are a key component to urban smog problems. Gasoline toxins reductions are an effective means of reducing human exposure risk to known and potential carcinogens. Benzene, a known human carcinogen contributes a significant fraction of the regulated emissions of toxins.

This paper examines the potential of ether oxygenates to reduce benzene evaporative emissions. The ether oxygenates under study include: MTBE (methyl-*tert*-butyl ether), ETBE (ethyl-*tert*-butyl ether), and TAME (*tert*-amyl methyl ether). An experimental program was developed to measure vapor phase hydrocarbon concentrations for both oxygenated and non-oxygenated synthetic fuels. Although a synthetic gasoline blend is used in this work, we believe conclusions based on the experimental data will successfully carry-over to actual reformulated gasoline(RFG).

EXPERIMENTAL

Fuel Composition

High purity oxygenates were used in all fuel compositions to minimize any impact that volatile impurities may have on altering head-space composition. Each ether oxygenate was freshly distilled immediately prior to use. Test hydrocarbons were purchased from Aldrich Chemical Company and were used without additional purification. The reported purity of our test oxygenates were > 99.99 % MTBE, 99.9% ETBE (without anti-oxidant), and 98% TAME.

Each batch of test fuel, typically 25 - 50 ml, was carefully blended so that the overall blending vapor pressure would be approximately 6.0 psi, assuming ideality. Total aromatic concentration in the blend is fixed at 20% toluene and 1% benzene to

simulate the RFG requirement of 1995. The three oxygenated fuels outlined in Table No. 1 were blended to contain 2.7 wt. % oxygen from the addition of either MTBE, ETBE, or TAME.

Table No. 1 Liquid Fuel Compositions

| Fuel Oxygenate | Components | Composition (Vol.%) | Blending Vapor Pressure (Psi @ 100°F) |
|----------------|------------|---------------------|---------------------------------------|
| Base | Toluene | 20.0 | 5.87 |
| | Benzene | 1.0 | |
| | 2,3-DMB | 79.0 | |
| MTBE | Toluene | 20.0 | 5.98 |
| | Benzene | 1.0 | |
| | 2,3-DMB | 64.0 | |
| | MTBE | 15.0 | |
| ETBE | Toluene | 20.0 | 5.88 |
| | Benzene | 1.0 | |
| | 2,3-DMB | 37.0 | |
| | 2,2-DMB | 25.0 | |
| | ETBE | 17.0 | |
| TAME | Toluene | 20.0 | 5.91 |
| | Benzene | 1.0 | |
| | 2,3-DMB | 27.0 | |
| | 2,2-DMB | 35.0 | |
| | TAME | 17.0 | |

DMB = Dimethylbutane

Vapor Generation

A schematic diagram of the Micro Head-Space vapor generating apparatus is shown in Figure No. 1. Approximately 25 ml of fuel to be tested is placed in a clean and dry 100 mL volumetric flask. The flask and contents are submersed in a temperature regulated water bath to insure accurate and uniform heat transfer. The volumetric flask is then fitted with a rubber septum through which is inserted a 1/8 inch stainless steel aerator line. This aerator is then attached to a metered ultra high purity helium delivery system. A metered amount of helium can be introduced into the head-space cavity, if necessary, to charge the sample loop. A thermocouple is inserted into the liquid through a second 1/8 inch Teflon® tube. Equilibrium head-space sample is carried through the sample port via diffusion. This fills the 0.3 mL sample loop contained in the Valco valve system. The entire system is placed in a constant temperature oven to reach equilibrium. After the desired temperature has been reached in the liquid fuel sample, one hour is allowed to reach equilibrium before a head-space sample is taken for gas chromatographic analysis.

Vapor Analysis

Effluent head-space sample is helium flushed from the sample loop through a pre-heated (120°F) 1/16 inch stainless steel line to the injector port of a Varian 3700 Gas Chromatograph. Hydrocarbon and oxygenate analysis is performed on a Hewlett Packard PONA 50 meter x 0.2 mm x 0.5 micron fused silica capillary column. Typical vapor analysis is carried out under isothermal conditions at 140°F. All data is collected and integrated for analysis on a Fisons Multichrom data acquisition system. The GC analysis was done a minimum of three times at each temperature. An average of the area percents was then calculated for each component present in the vapor sample.

A gas sample calibration standard was prepared and analyzed in the following manner. A precisely weighted liquid sample of all components was transferred to an evacuated one-liter round bottom flask, fitted with a Teflon® lined serum cap. We have experimentally determined that a Teflon® lined serum cap is required to prevent the

irreversible absorption of aromatic components into rubber septum. The flask contents are allowed to equilibrate at atmospheric pressure with ambient air to give a vapor sample of known concentration. The mass at atmospheric pressure was well below the components dew point. An aliquot of this vapor sample is then charged directly to the sample loop which had been thermally equilibrated to the temperature of the initial head-space experiment and then analyzed. Area percents determined in each temperature study were then converted to vapor mole percent.

DISCUSSION

Head-space concentrations were predicted at 80, 100, and 120°F using UNIFAC-Flash Simulations¹ on all four test fuels with an ASPEN PLUSTM computer software package. These results are shown in Graph No. 1.

An examination of the computer generated data reveals that all three oxygenates suppress the volatility of benzene in the 80 - 120°F temperature range. A linear suppression is predicted over the 40°F range for each oxygenate. Overall benzene evaporative emissions are reduced an average of approximately 15% over the temperature range with MTBE. TAME yields a benzene reduction of approximately 13%. ETBE yields the lowest benzene suppression of approximately 10%. This data from the model strongly suggests that the amount of benzene suppression is **dependent** upon the type of ether oxygenate used with minor temperature effects.

An examination of the experimental benzene head-space concentration measurements obtained in our Micro head-space apparatus is outlined in Graph No. 2. These experimental results reveal that benzene suppression is **independent** of the type of ether oxygenate used and dependent upon the test temperature. This data supports the contention that reduced benzene evaporative emissions is a generic trait characteristic of all ether oxygenates. At a constant 2.7 wt.% oxygen content, benzene evaporative emissions were reduced an average of 14%, independent of the ether oxygenate structure. In general, there is a linear increase (approximately 8%) in the amount of benzene found in the head-space during a 40°F temperature increase. This trend is in line with our simplistic model of colligative polar solution interactions between ether oxygenates with aromatics which is manifested in lower benzene evaporative emissions. As the temperature is increased, solution molecules acquire sufficient kinetic energy which in turn increases volatility by weakening the colligative interaction.

CONCLUSIONS

Benzene evaporative emission reduction averaged approximately 14% for fuels containing 2.7 wt.% oxygen in the 80 - 120°F range

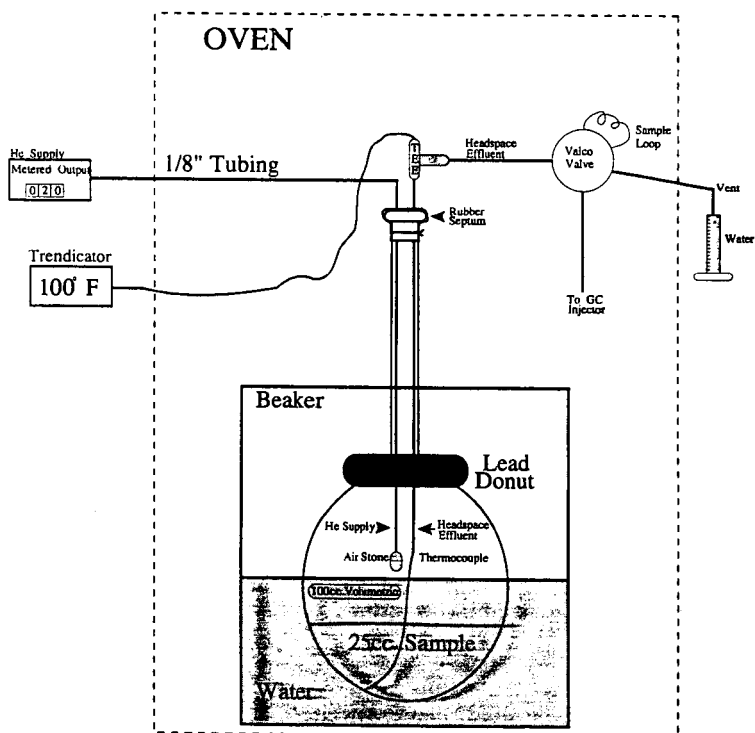
Reduced benzene evaporative emissions from an oxygenated fuel appear to be independent of the ether oxygenate molecular structure

LITERATURE CITED

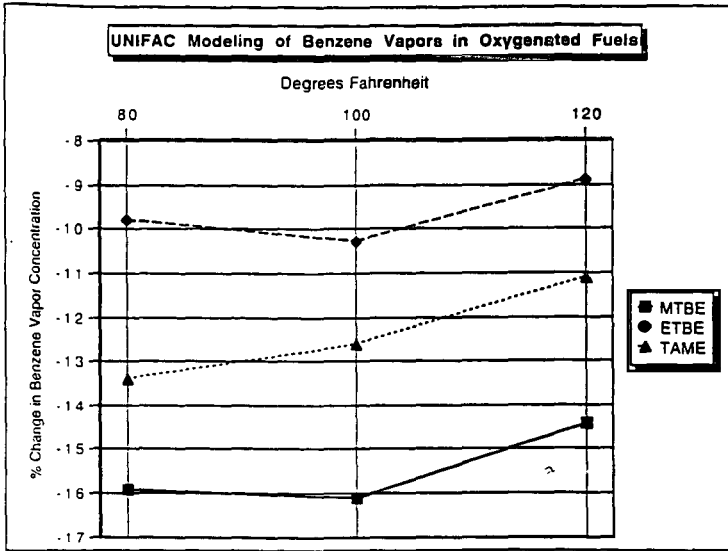
1. A. Fredenslund, J. Gmehling, and P. Rasmussen, **Vapor-Liquid Equilibria Using UNIFAC, A Group Contribution Method**, Elsevier, Amsterdam, 1977.

Figure No. 1

Micro Head-Space Testing Apparatus



GRAPH No. 1



GRAPH No. 2

